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Rotary Kiln Heat Balance.

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IN order to exercise proper control over burning conditions in kilns, to compare results from one kiln, or plant, with another, or for other purposes including design, etc., it is necessary to know how the heat applied is used, and in this article it is shown how what may be called the " Ultimate " Heat Balance may be calculated. This makes no particular allowance for certain heat exchanges occurring inside the kiln which are, at any rate to a certain extent, recuperative; it but shows how the heat used may be divided mainly from consideration of external measurements.

The principal heat losses or manner in which heat is used are :

(1) Slurry or raw meal is dried and the contained water evaporates and is superheated to the exit-gas temperature.

(2) Carbonates of lime and magnesia are decomposed.

(3) The CO_2 which is evolved may be considered as being heated to the exit-gas temperature.

(4) The gases formed from the combustion of the fuel used still contain heat when discharged from the kiln at the exit-gas temperature.

(5) Any excess air used above that required for consumption will be heated to the exit-gas temperature.

(6) Any CO present due to imperfect combustion represents a loss of heat.

(7) The moisture contained by the coal as fired (or as dried in cases where the air from the drier goes to the kiln) is evaporated and superheated to the exit-gas temperature.

(8) The clinker formed by reaction between the constituents so formed is heated to the temperature at which it leaves the kiln. Heat losses from the

clinker cooler are represented by the equation cooler losses = heat in clinker leaving kiln minus heat in clinker leaving cooler minus heat in preheated air (provided this passes eventually to the kiln; if used for coal drying or grinding there may be additional heat losses).

(9*a*) The air used for combustion always contains varying quantities of water as vapour, depending on relative humidity and temperature, and this moisture is heated to the exit-gas temperature.

(9*b*) Dust carried out of the kiln by the gases carries out heat according to the temperature of these gases. There may also be some loss due to partial decarbonation of this dust, in addition to that in (2).

(9*c*) There are losses through the kiln shell and hood by convection and radiation due to its temperature being higher than its surroundings.

(9*d*) Certain constituents of the raw materials which contain combined water are dehydrated and decomposed, the water being vaporised and superheated to the exit-gas temperature.

(9*e*) Where organic matter is present in the raw material this is consumed in the kiln, requiring air for combustion. A residue of nitrogen is left, which must be heated to the exit-gas temperature.

The following are the sources from which heat is supplied to the kiln :

(1) From combustion of the fuel used.

(2) From heat regenerated from the clinker after leaving the kiln, and contained in the preheated air.

(3) Combustion of any organic matter in the raw materials.

(4) From the exothermic reaction during combination between the constituents of the raw materials after decarbonisation has taken place.

The best datum from which the bulk of these heat values should be calculated is, for the sake of simplicity, the average temperature of the atmosphere, which in England may be taken at 60 deg. F. without serious error.

From the equation given in par. (8), by transposition, heat in clinker leaving kiln = heat in clinker leaving cooler plus heat in preheated air plus cooler losses. This may therefore be substituted for (8), and as " heat in preheated air " now appears on both sides of the Heat Balance (i.e., No. 8 in " losses " and No. 2 in " gains ") it may be eliminated.

As " Cooler losses " and " Kiln radiation losses " are difficult to estimate accurately, although measurement of the shell temperature at a considerable number of points throughout its length, and calculation from the laws of radiation and convection, will allow of its approximate determination if the " emissivity coefficient " of the surface and the influence of the surroundings can be taken into account, these items, together with other small items where values are not known with sufficient accuracy (e.g., losses Nos. 9*a*, *b*, *c*, *d* and *e*), may be grouped under the heading " Losses unaccounted for."

The simplified Heat Balance will then appear as follows, and it will be found to answer very well for comparative purposes:

Dr.	Cr.
(1) Heat required to evaporate and superheat slurry moisture.	(1) Heat due to calorific value of fuel.
(2) Heat required for decomposition of carbonates.	(2) Heat due to exothermic reaction of clinker formation.
(3) Heat lost in CO_2 from raw material.	(3) Heat due to combustion of organic matter, etc., in raw material.
(4) ,, ,, ,, combustion gases.	
(5) ,, ,, ,, excess air.	
(6) ,, ,, ,, CO due to imperfect combustion.	
(7) ,, ,, ,, coal moisture.	
(8) ,, ,, ,, clinker leaving cooler.	
(9) Losses unaccounted for (obtained by difference).	

The two sides will necessarily balance, and the Heat Balance may then be used as desired.

As indicated, item No. 9 (Dr. side) includes: Radiation losses of kiln and cooler (also convection losses); heat lost through dehydration and dissociation (of clayey constituents) of raw materials; heat lost through moisture in air used for combustion being heated to exit-gas temperature; heat lost through dust in gases at exit-gas temperature; heat lost through nitrogen from air used for combustion of organic matter, etc., being heated to exit-gas temperature (now, however, allowed for under "organic matter"); heat lost through products of combustion of organic matter being heated to exit-gas temperature; heat lost through decomposition of carbonates included in dust losses, etc. Where any of these values can be calculated with any accuracy they may be included as separate items. Approximations may well be made for the last three, as they are small and considerable errors will have little relative effect.

The Heat Balance may be calculated in any units desired, or converted from one set of units to another. In the following calculations values are calculated to B.T.U. per 100 lb. of clinker produced. This may easily be converted to, e.g.

Per cent. of standard coal to clinker ("standard coal" is a theoretical dry coal having calorific value of 7,000 calories per gram or 12,600 B.T.U. per lb.) .. .. Divide B.T.U. by 12,600

B.T.U. per barrel: multiply B.T.U. by 3.76 (at 376 lb. per barrel).

Kg. calories per kg.: divide B.T.U. by 1.8.

Per cent. of total coal used, etc.: divide B.T.U. by 126 × per cent. of coal to clinker.

For convenience, it may be found desirable to have sheets printed giving spaces for the necessary data from which the various items may be calculated, together with the Heat Balance values, and a specimen is shown in Fig. 1.

The method of calculating the various heat quantities of the Heat Balance shown in Fig. 1 is:

(1) Heat Required to Evaporate and Superheat Slurry Moisture

Data required: Slurry moisture, per cent.; slurry $CaCO_3$, per cent.; exit-gas temperature; B.T.U. per lb. water vapour.

ROTARY KILN HEAT BALANCE.

Date—Period ending						
KILNS.						
Kiln exit-gas temperature, deg. F.						
,, ,, CO_2, per cent. ..						
,, ,, O_2 ,, ..						
,, ,, CO ,, ..						
Temperature of clinker leaving cooler, deg. F.						
Water in slurry, per cent. ..						
$CaCO_3$ in dried slurry, per cent. ..						
Water in raw coal, per cent. ..						
Standard coal factor						
Excess air, per cent.						
Coal consumption, actual						
Coal consumption, gas analysis						
HEAT BALANCE.	PER CENT. STANDARD COAL TO CLINKER.					
CO_2 ex raw materials						
Water ex raw materials						
Gases of combustion						
Excess air						
H_2O in coal						
CO in exit gases						
Dust and air moisture						
Dissociation of carbonates ..						
Heat in clinker leaving cooler ..						
Total heat accounted for						
Balance unaccounted for						
TOTALS						
CREDIT.						
Coal calorific value						
Exothermic reaction						
Organic matter in slurry						
TOTALS						

FIG. 1.

We may most conveniently deal first with the heat quantities contained in 1 lb. of all the gases concerned at varying temperatures. Dr. Martin, in "Chemical Engineering applied to the Cement Rotary Kiln," gives (chap. ii, p. 2) a table showing the instantaneous specific heats of CO_2, N_2, H_2O, and air at various temperatures. Taking these between the limits of 200 deg. F. to 1,500 deg. F., we obtain the following equations for the specific heat of each gas:

T deg. F. = gas temperature.

Specific heat (instantaneous) $CO_2 = 0.1987 + 8.17 \times 10^{-5}T - 15.1 \times 10^{-9}T^2$

" " $H_2O = 0.4701 - 21.3 \times 10^{-6}T + 355 \times 10^{-10}T^2$

" " $N_2 = 0.2344 + 21 \times 10^{-6}T$

" " Air $= 0.2279 + 2 \times 10^{-5}T$.

Obviously the instantaneous specific heat of any material is the rate of increase in heat contained (or required) for a small increment in temperature, i.e.,

Where S = instantaneous specific heat

Q = heat quantity in 1 lb. of gas

$$\frac{dQ}{dT} = S$$

Then $Q = \int S dT$.

Carrying out this integration between the limits of 60 deg. F. (the datum temperature) and T deg. F. (exit-gas temperature) we obtain

QT deg. 60 deg. $CO_2 = 0.1987T + 40.85 \times 10^{-6}T^2 - 50.3 \times 10^{-10}T^3 - 12.068$ B.T.U.

" " $H_2O = 1029.7 + 0.4701T - 10.65 \times 10^{-6}T^2 + 118.3 \times 10^{-10}T^3$ B.T.U.

" " $N_2 = 0.2344T + 10.5 \times 10^{-6}T^2 - 14.1$ B.T.U.

" " Air $= 0.2279T + 10 \times 10^{-6}T^2 - 13.71$ B.T.U.

It will be noted that in the case of H_2O the latent heat of evaporation has been included. Dr. Martin gives (chap. 12, p. 4) 1057.9 B.T.U. per lb. of steam at 60 deg. F. condensed to water at 60 deg. F.

The next requirement is the quantity of water to be evaporated and heated per 100 lb. clinker.

Let slurry moisture = M per cent.

" $CaCO_3$ = C "

" $MgCO_3$ = m "

" loss on ignition = 1 "

" combined water = a "

" organic matter = p "

Dust losses = d per cent. of clinker (assumed to be dry slurry)

Standard coal consumption = N per cent. of clinker.

Coal ash absorbed in clinker = A_1 per cent. of coal.

Then $1 = \frac{44}{100} \times C + \frac{44}{84} \times m + a + p$

$1 = 0.44\,C + 0.524\,m + a + p$

100 lb. clinker contains $0.01\,NA_1$ lb. of coal ash.

Then raw material required for 100 lb. of clinker $= d + \frac{10{,}000 - NA_1}{100 - 1}$ lb.

and water to be evaporated $= \frac{M}{100 - M}\left(d + \frac{10{,}000 - NA_1}{100 - 1}\right)$ lb.

As a close approximation the following equation will be found satisfactory for most purposes, allowing average ash and coal consumptions.

Water evaporated $= \frac{M}{100 - M} \times \frac{22{,}720}{221 - C}$ lb. per 100 lb. clinker.

Multiply this weight of water by the heat quantity for the appropriate exit-gas temperature, i.e.,

$$Q = 1029.7 + 0.4701T - 10.65 \times 10^{-6}T^2 + 118.3 \times 10^{-10}T^3,$$

to obtain the B.T.U. per 100 lb. clinker lost by reason of the evaporation of the water in the slurry. Tables I and II show the weight of water in slurry at various moistures and percentages of $CaCO_3$, and B.T.U. per lb. of water vapour at various temperatures.

TABLE I.

WEIGHT OF SLURRY WATER PER 100 LB. CLINKER (INCLUDES APPROXIMATELY 2 LB. DUE TO DUST FORMATION).

Per cent. Moisture in Slurry.

Per cent. $CaCO_3$	34	35	36	37	38	39	40	41	42	43
74.0	79.60	83.20	86.95	90.75	94.70	98.80	103.00	107.40	111.90	116.60
74.5	79.90	83.50	87.25	91.10	95.05	99.15	103.35	107.75	112.30	117.00
75.0	80.20	83.80	87.55	91.40	95.40	99.50	103.70	108.10	112.70	117.40
75.5	80.45	84.10	87.85	91.70	95.70	99.85	104.10	108.50	113.10	117.80
76.0	80.70	84.40	88.15	92.00	96.00	100.20	104.45	108.85	113.50	118.20
76.5	81.00	84.65	88.45	92.30	96.35	100.55	104.80	109.20	113.90	118.60
77.0	81.30	84.95	88.75	92.65	96.70	100.90	105.15	109.60	114.25	119.00
77.5	81.60	85.20	89.10	93.00	97.05	101.25	105.50	110.00	114.65	119.40
78.0	81.85	85.55	89.40	93.30	97.40	101.60	105.90	110.40	115.05	119.85
78.5	82.15	85.85	89.70	93.65	97.70	101.95	106.25	110.75	115.50	120.30
79.0	82.40	86.15	90.00	94.00	98.05	102.30	106.65	111.10	115.90	120.70

TABLE II.

B.T.U. IN 1 LB. OF WATER VAPOUR AT VARIOUS TEMPERATURES (FROM 60 DEG. F.)

Deg. F.	0	20	40	60	80
200	1123.4	1132.7	1142.1	1151.4	1160.8
300	1170.1	1179.4	1188.8	1198.1	1207.4
400	1216.8	1226.1	1235.5	1244.8	1254.2
500	1263.6	1272.9	1282.3	1291.7	1301.1
600	1310.5	1319.9	1329.3	1338.7	1348.1
700	1357.6	1367.0	1376.5	1386.0	1395.5
800	1405.0	1414.5	1424.1	1433.6	1443.2
900	1452.8	1462.4	1472.1	1481.7	1491.3
1,000	1501.0	1510.7	1520.5	1530.2	1539.9
1,100	1549.7	1559.5	1569.3	1579.2	1589.0
1,200	1598.9	1608.8	1618.7	1628.8	1638.8

(2) Heat Required for Decomposition of Carbonates

The heat of dissociation of $CaCO_3$ and $MgCO_3$ is first required. Several values are given in cement literature. Dr. Martin in his book, already mentioned, quotes 774 B.T.U. per lb. $CaCO_3$ decomposed as the particular value taken at present, and 756 B.T.U. per lb. $CaCO_3$ as calcite, which is the usual form in cement raw materials. He points out, however, that the heat of dissociation varies with the temperature (or pressure) at which decomposition takes place, and derives, from the vapour pressure—temperature consideration results varying from 682 to 700 B.T.U. as the probable dissociation temperatures in the rotary kiln.

Dr. Hans Bussmeyer (CEMENT AND CEMENT MANUFACTURE, Jan., 1932) and W. Eitel and H. E. Schweite (B.S.A., No. 1821, 1932) give $CaCO_3$ 765 B.T.U. per lb. $CaCO_3$ and $MgCO_3$ 387 B.T.U. per lb. $MgCO_3$. These appear to be based on calorimetric determinations.

" International Critical Tables " (Vol. V) give values for the heat of formation of compounds from these elements, from which the heat of dissociation may be calculated. These result in the values $CaCO_3$, 769.6 B.T.U. per lb.; $MgCO_3$, 582 B.T.U. per lb.

Calculation of the heat of dissociation of $MgCO_3$ from the vapour pressure—temperature equation given by Dr. Martin gives the value 479.6 B.T.U. per lb. There is thus considerable divergence, particularly in the case of $MgCO_3$. Fortunately, however, this constituent is usually small so that errors are not likely to be serious. In this paper the values taken are $CaCO_3$, 756 B.T.U. per lb.; $MgCO_3$, 387 B.T.U. per lb.

The quantity of carbonates which are decomposed must now be found. Using the same notation as in the previous section, the quantity of raw material which goes to make 100 lb. of clinker is

$$\frac{10{,}000 - NA_1}{100 - 1} \text{ lb.}$$

Then the quantity of $CaCO_3$ decomposed

$$= \frac{C}{100} \times \frac{10{,}000 - NA_1}{100 - 1} \text{ lb. per 100 lb. clinker,}$$

and the quantity of $MgCO_3$ decomposed

$$= \frac{m}{100} \times \frac{10{,}000 - NA_1}{100 - 1} \text{ lb. per 100 lb. clinker.}$$

A close approximation for most normal cases is given by

$$CaCO_3 = \frac{223\,C}{221 - C} \text{ lb. per 100 lb. clinker}$$

$$MgCO_3 = 1.5\,m \text{ lb. per 100 lb. clinker}$$

again allowing for average ash and coal consumptions where C and m are a percentage of $CaCO_3$ and $MgCO_3$ respectively in the raw materials.

Multiplying these quantities by the B.T.U. per lb. gives

Decomposition of $CaCO_3$ requires

$$756 \times \frac{223\,C}{221 - C} = \frac{168{,}590\,C}{221 - C} \text{ B.T.U. per 100 lb. clinker.}$$

Decomposition of $MgCO_3$ requires

$$387 \times 1.5\,m = 580\,m \text{ B.T.U. per 100 lb. clinker.}$$

TABLE III.

B.T.U. REQUIRED FOR DECOMPOSITION OF $CaCO_3$ PER 100 LB. CLINKER.

Per cent. $CaCO_3$.	B.T.U.	Per cent. $CaCO_3$.	B.T.U.
74.0	84,867	77.0	90,148
74.5	85,732	77.5	91,049
75.0	86,603	78.0	91,957
75.5	87,480	78.5	92,871
76.0	88,363	79.0	93,791
76.5	89,252		

(Add 580 m to allow for $MgCO_3$.)

(3) Heat Lost in CO_2 from Raw Materials

We have already found that the weight of $CaCO_3$ and $MgCO_3$ is given by approximately

$$CaCO_3 = \frac{223\,C}{221 - C} \text{ lb. per 100 lb. clinker.}$$

$$MgCO_3 = 1.5\,m \text{ lb. per 100 lb. clinker.}$$

1 lb. $CaCO_3$ evolves 0.44 lb. CO_2.

1 lb. $MgCO_3$ evolves 0.524 lb. CO_2.

$$\text{Then } CO_2 \text{ per 100 lb. clinker} = 0.44 \times \frac{223\,C}{221 - C} + 0.524 \times 1.5\,m$$

$$= \frac{98.1\,C}{221 - C} + 0.79\,m.$$

TABLE IV.

CO_2 PER 100 LB. CLINKER (FROM RAW MATERIALS).

Per cent. $CaCO_3$.	Lb. CO_2.	Per cent. $CaCO_3$.	Lb. CO_2.
74.0	49.40	77.0	52.45
74.5	49.90	77.5	53.00
75.0	50.40	78.0	53.50
75.5	50.90	78.5	54.00
76.0	51.40	79.0	54.55
76.5	51.90		

(Add 0.79 × per cent. $MgCO_3$.)

The heat contained by 1 lb. CO_2 has been given previously. It is expressed in B.T.U. by the equation

$$QCO_2 = 0.1987\,T + 40.85 \times 10^{-6}T^2 - 50.3 \times 10^{-10}T^3 - 12.068.$$

Table V has been calculated from this equation. Multiply the weight of CO_2 per 100 lb. clinker by the heat content in B.T.U. to obtain the heat losses for the CO_2 in the raw material at the exit-gas temperature.

TABLE V.

B.T.U. PER LB. CO_2 FROM 60 DEG. F.

Deg. F.	0	20	40	60	80
200	29.3	33.6	37.9	42.3	46.7
300	51.1	55.5	60.0	64.5	69.0
400	73.6	78.2	82.8	87.5	92.2
500	96.9	101.6	106.4	111.2	116.0
600	120.8	125.6	130.5	135.4	140.3
700	145.3	150.3	155.3	160.3	165.4
800	170.5	175.6	180.7	185.8	191.0
900	196.2	201.4	206.6	211.9	217.2
1,000	222.5	227.8	233.1	238.5	243.9
1,100	249.3	254.7	260.1	265.6	271.1
1,200	276.6	282.1	287.6	293.2	298.8

(4) Heat Losses in Combustion Gases

The requirements for this calculation are : (*a*) Lb. of coal consumed per 100 lb. clinker ; (*b*) weight of products of combustion of 1 lb. of coal ; and (*c*) heat content of combustion gases.

To obtain (*b*) it is necessary to know the ultimate analysis of the coal used. Unfortunately this is not often carried out in the cement works laboratory ; in such cases, and where a bituminous coal is used, the values given later for South Yorkshire coal may be accepted with little error. This example will serve to show the method of calculating the combustion gases from the ultimate analysis, a process familiar to chemists. It is most convenient to convert the raw coal analysis to standard coal, this being a theoretical standard of dry coal having a calorific value of 7,000 calories, or 12,600 B.T.U. This has been done, for a coal containing 10 per cent. of water as received and 6,610 calories as dry coal, by multiplying the items (except ash) by

$$\frac{7{,}000 \times 100}{6{,}610\,(100 - 10)} = \frac{1}{0.85}$$

What is known as " the standard coal factor " is here shown to be 0.85. The ash is obtained by difference.

ANALYSIS OF SOUTH YORKSHIRE COAL.

	Raw Coal.	Standard Coal.	
Moisture (as received) ..	10.0	—	
Carbon	62.5	73.5	
Hydrogen	4.0	4.7	
Nitrogen	1.2	1.4	
Sulphur	1.6	1.9	
Oxygen	6.4	7.5	
Ash	14.3	11.0	
	100.0	100.0	
Calorific value (as dry) ..	6,610	7,000	calories
Standard coal factor	0.85		

The products of combustion will comprise

$$CO_2 = C \times \frac{44}{12} = 0.735 \times \frac{44}{12} = 2.695 \text{ lb. per lb. standard coal.}$$

$$SO_2 = S \times \frac{64}{32} = 0.019 \times 2 = 0.038 \text{ lb. per lb. standard coal.}$$

$$H_2O = H \times \frac{18}{2} = 0.047 \times 9 = 0.423 \text{ lb. per lb. standard coal.}$$

$N_2 = 0.014 + N_2$ contained by air used for combustion.

This is calculated as follows: Find total O_2 required for

$$CO_2 = C \times \frac{32}{12} = 1.960 \text{ lb. per lb. standard coal.}$$

$$SO_2 = S \times \frac{32}{32} = 0.019 \text{ lb. per lb. standard coal.}$$

$$H_2O = H \times \frac{16}{2} = 0.376 \text{ lb. per lb. standard coal.}$$

Deduct O_2 in coal $= 0.075$ lb. per lb. standard coal.

Total O_2 required $= 2.280$ lb. per lb. standard coal.

Since nitrogen is present in the combustion air to the extent of $\frac{77}{23}$ times the oxygen, then

N_2 in air required $= 2.28 \times \frac{77}{23} = 7.64$ lb. per lb. standard coal

add N_2 in coal .. .. 0.014 lb. per lb. standard coal

Total N_2 .. $= 7.654$ lb. per lb. standard coal.

In adding these figures a total of 10.81 lb. of combustion gases results from the burning of 1 lb. of standard coal comprising CO_2, 2.695 lb.; SO_2, 0.038 lb.; H_2O, 0.423 lb.; N_2, 7.654 lb.; total, 10.810 lb.

The air required for combustion of 1 lb. standard coal = 2.28 lb. oxygen and 7.64 lb. nitrogen = 9.92 lb.

HEAT CONTENT OF COMBUSTION GASES.

$QCO_2 = 0.1987\ T + 40.85 \times 10^{-6} T^2 - 50.3 \times 10^{-10} T^3 - 12.068$ B.T.U. per lb. CO_2.

Then per lb. standard coal $= 2.695\ QCO_2$ B.T.U.

The specific heat of SO_2 may be taken as 0.154, as only a small quantity is present. Then

$QSO_2 = 0.154\ (T - 60)$ B.T.U. per lb. SO_2

per lb. standard coal $= 0.038 \times 0.154\ (T - 60)$ B.T.U.

$QH_2O = 1029.7 + 0.4701\ T - 10.65 \times 10^{-6} T^2 + 118.3 \times 10^{-10} T^3$ B.T.U. per lb. H_2O

per lb. standard coal $= 0.423\ QH_2O$.

$QN_2 = 0.2344\ T + 10.5 \times 10^{-6} T^2 - 14.1$ B.T.U. per lb. N_2

per lb. standard coal $= 7.654\ QN_2$.

By multiplying and adding these quantities, we obtain the following expression for the heat quantity in B.T.U. lost in the combustion gases from 1 lb. standard coal at the exit-gas temperature T deg. F. (Table VI is calculated from this equation):

Q (combustion gas) $= 294.5 + 2.535\ T + 186 \times 10^{-6}T^2 - 85.5 \times 10^{-10}T^3$ B.T.U. per lb. standard coal.

TABLE VI.

B.T.U. PER LB. STANDARD COAL IN GASES OF COMBUSTION, FROM 60 DEG. F.

Deg. F.	0	20	40	60	80
200	808.9	861.1	913.5	966.0	1018.7
300	1071.5	1124.5	1177.6	1230.9	1284.3
400	1337.7	1391.3	1445.1	1499.0	1553.1
500	1607.4	1661.7	1716.2	1770.8	1825.6
600	1880.6	1935.6	1990.8	2046.1	2101.6
700	2157.2	2212.9	2268.8	2324.8	2380.9
800	2437.2	2493.6	2550.1	2606.8	2663.6
900	2720.4	2777.4	2834.6	2891.9	2949.4
1,000	3007.0	3064.7	3122.5	3180.4	3238.5
1,100	3296.7	3355.0	3413.4	3472.0	3530.7
1,200	3589.6	3648.5	3707.6	3766.8	3826.1

The heat loss due to gases of combustion is found by multiplying the percentage of standard coal to clinker (i.e., lb. standard coal per 100 lb. clinker) by the heat quantity in B.T.U. for the appropriate exit-gas temperature. It will be found that for bituminous coals, when converted to a standard coal basis, the quantity of heat contained by the gases of combustion varies little from the example given, and these figures may be adopted where the correct ultimate analysis is unknown. As examples we may quote the coal analyses given by Dr. Martin in Chap. 10 of his book:

	Coal A. Per cent.	Coal B. Per cent.	
Carbon	65.86	72.20	
Hydrogen	4.55	4.99	
Sulphur	1.37	1.18	
Ash	19.76	17.23	
Oxygen	7.06	2.97	
Nitrogen	1.40	1.43	
Calorific value	11,851	12,710	B.T.U.
Combustion gases per lb. standard coal.			
CO_2	2.562	2.624	
H_2O	0.436	0.448	
N_2	7.271	7.669	

Heat quantity in B.T.U. per lb. standard coal:

	Coal A.	Coal B.	South Yorkshire Coal.
500 deg. F. ..	1,631	1,568	1,607
1,000 deg. F. ..	3,027	2,903	3,007

Coal A shows a variation of + 1½ per cent. at 500 deg. and + ⅝ per cent. at 1,000 deg., and Coal B a variation of — 2½ per cent. at 500 deg. and — 3½ per cent. at 100 deg. These differences are comparable with experimental errors in obtaining the data for the Heat Balance, and even the largest will only represent about 25 to 35 B.T.U. per lb. of clinker.

(To be continued.)

Recent Patents Relating to Cement.

384,060. — **Cement Manufacture.** Gill, H. A., 51, Chancery Lane, London. (Smidth & Co., Aktieselskab, F. L., 33, Vestergade, Copenhagen.) Nov. 16, 1931.

In the manufacture of cement, lime, etc., in a rotary kiln, the calcination of the charge is effected in a chamber outside the kiln by direct contact with heat-transmitting material, e.g., a portion of the charge material, or pieces of fireclay or porcelain, which has been previously heated by the waste gases from the kiln. In the construction shown in Fig. 2 the calcining chamber comprises a rotary drum (2) to which raw material from the upper end of the kiln (1) pipe 26 may be uncontaminated by products of combustion a valve (9) is provided for preventing direct communication between the chamber (2) and kiln (1).

Fig. 3 shows a modification in which the heat-transmitting material is constituted by the coarser part of the charge, this coarse material being heated by the waste gases in a shaft (40) and then passing downwardly through the upper part of the kiln to conduits (27) delivering to a number of calcining chambers (2') arranged round the kiln and rotating therewith. The raw charge is fed to each of the chambers (2') through a chute (32) and head (31),

FIG.2.

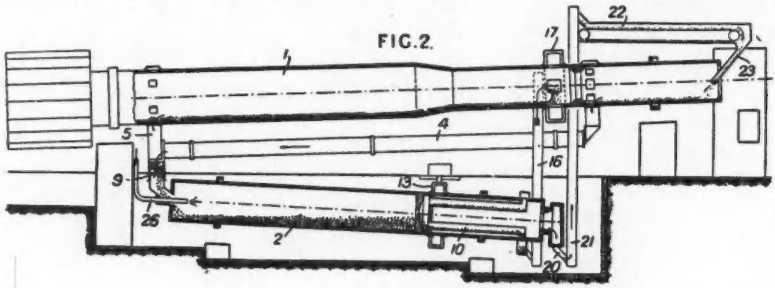
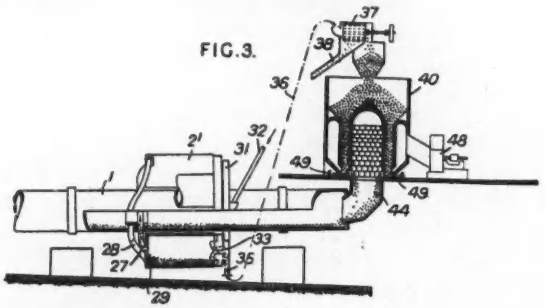


FIG.3.



Cement Manufacture.

and highly heated material from a hotter zone thereof are supplied through conduits 4, 5 respectively. The lower end of the drum (2) constitutes a preheater for the raw charge, the outgoing hot calcined material traversing the tubes (10) around which the raw charge passes from the charging opening (13) to the outlet (20). The raw charge thus preheated is conveyed to the upper end of the kiln by elevator (21), conveyor (22), and chute (23), while the calcined material from the drum (2) is reintroduced at 17 into the kiln by an elevator (16). The portion of the kiln charge not taken off by the conduit (5) passes on to the sintering zone of the kiln. In order that the carbon dioxide taken off from the chamber (2) through and, after calcination by contact with the hot coarse material, passes through grid (29) and enters the kiln through conduit (28). The coarse material accumulates in the chambers (2') from which it eventually escapes through a cylindrical sieve (33) to an outlet (35), an elevator (36) being provided for delivering the discharged material to a sieve (37). The fines from this sieve are delivered by a chute (38) to the chute (32), while the coarse material passes to the shaft (40). The latter comprises an annular passage down which the material travels and through which the hot kiln gases are drawn by a fan (48). Pushers (49) deliver the material thus heated to a chute (44) leading to the upper end of the kiln.

Effect of Composition of Portland Cement on Heat Evolved during Hardening.

A PAPER by Messrs. Hubert Woods, Harold H. Steinour, and Howard R. Starke, of the Riverside Cement Company, California, in a recent number of "Industrial and Engineering Chemistry," presents a study of the heat evolution during the hardening of Portland cements of varied composition. Heat of hardening is here defined as the total quantity of heat evolved from the time of addition of the gauging water until the end of the periods for which it is given. This property is of interest in the construction of massive works such as dams, in which the great thicknesses severely hinder the outflow of the heat. The consequent rise in temperature while the cement is hardening may result in contraction and cracking when the eventual cooling to the surrounding temperature takes place. The compositions of the cements prepared for this work were varied over a wide range with a view to bringing out the essential factors governing heat evolution. The heat evolutions were determined over various intervals of time up to 180 days, using for this purpose samples of neat cement made up to a water content of 40 per cent. of the weight of cement, and stored at 95 deg. F.

The amounts of heat evolved by the hardening cement pastes, from the time of mixing up to the time of test, were determined indirectly from the heats of solution of the various samples in an acid solvent. This determination is based on Hess's law of constant heat summation: The change in heat content of a system in passing from one state to another is independent of the path whereby the passage is made. As applied to the present work, this method requires a determination of (1) the heat of solution of the cement in its initial state (that is, unreacted), (2) the heats of solution of the cement after reaction with water for various lengths of time, and (3) the difference between the two quantities to obtain the value of the heat evolved on hardening.

Calorimeter Design

The heats of solution of the various samples were determined in a calorimeter designed especially for this purpose. The calorimeter, shown in Fig. 1, is composed of the following essential elements: A cylindrical copper vessel of about 1,200 ml. capacity, lined with pure gold, and chromium plated and polished on the outside. A tight-fitting cover for the vessel, plated and polished on top and covered with Bakelite varnish on its lower surface. A cylindrical brass outer jacket completely surrounding the inner reaction vessel, chromium plated and polished inside, and fitted with a removable water-tight cover. This cover is fitted with several chimneys, as follows: One admits the stem of a Beckmann thermometer, which passes also through a gasketed opening in the lid of the reaction vessel and into the liquid therein. Another contains two ball bearings holding a shaft for the purpose of driving a propeller stirrer in the inner vessel. A third chimney admits the stem of a funnel through which

the powdered sample is introduced. A fourth carries insulated wires leading to the heater coil. An electrical heating coil of about 50 ohms resistance, sealed between two brass tubes which surround the propeller stirrer, serves to direct the circulation. The entire heater unit is mounted vertically by three brass legs whose upper ends are fastened to the lid of the reaction vessel. The wires leading to the heater element pass out through one of these legs. The entire heater element is protected from attack by acid by a well-baked coating of Bakelite varnish.

The primary purpose of the heater is to permit a determination of the effective heat capacity of the reaction vessel and contents. It also serves as a means of temperature adjustment upwards to the desired value before commencing a determination of heat of solution. A bank of storage cells, a

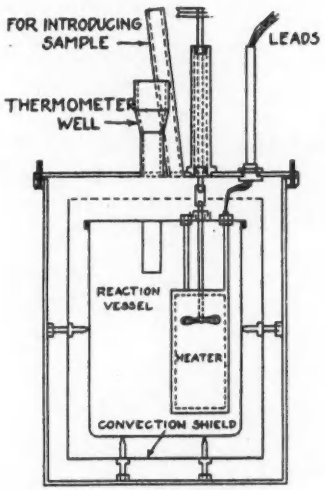


Fig. 1.

potentiometer, galvanometer, standard cell, volt box, and standard resistance comprise the energy source and means of measuring the energy input to the calorimeter.

All temperature changes were measured with Beckmann thermometers. After setting up the calorimeter, it was submerged completely, except for the upper parts of the chimneys, in a water thermostat controlled automatically to ±0.003 deg. C. Temperatures of this water bath were observed frequently during each test. Time intervals during calibration tests, and during the rapid rise part of a determination of heat of solution, were measured on a chronograph. Where the rate of temperature change was low, as before and after the rapid rise due to addition of the sample, time intervals were measured by

a watch. The solvent used throughout this investigation was an aqueous solution of 2 *N* nitric acid and 0.25 *N* hydrofluoric acid.

Preparation of Clinkers

Raw mixtures were prepared by adding to portions of a finely ground commercial kiln feed such quantities of ground technical oxides and carbonates as would bring the compositions to the desired values. The mixtures were made homogeneous by rolling on a cloth and by milling in a small laboratory batch mill until the fineness was such that over 92 per cent. would pass the 200-mesh sieve. Each mixture was mixed with sufficient water to give a reasonably plastic mass, formed into bars, and thoroughly dried at about 120 deg. C. The dried bars were stacked checkerwork fashion in a gas-fired down-draught stationary furnace designed to maintain a uniform temperature. The temperature of each charge during firing was frequently observed by an optical pyrometer sighted on the charge through a hole in the furnace wall. The temperatures were maintained at the desired values within ±15 deg. C.

The temperatures chosen for firing were determined from tests in a small gas-fired muffle furnace. For each composition there was thus determined the temperature at which combination of the lime was practically complete, and this information was used as a guide in choosing proper firing temperatures for the large furnace.

In all cases the total firing time was three hours. One hour was taken to bring the charge up to the desired temperature, and this temperature was then maintained for two hours. At the end of the test the fire was shut off, and the furnace and charge allowed to cool overnight. The clinker was removed from the furnace, crushed, and ground in a disc pulveriser to approximately −20 mesh. A sample was taken for analysis after thorough rolling, and the remainder was stored in tightly closed cans.

Preparation of Cements

The clinkers prepared as described were ground in a small batch mill, together with amounts of fine C. P. gypsum calculated to give 1.5 per cent. SO_3 in the resulting cements (except in cases where it was desired to have a higher sulphate content in the cement). Finenesses were determined on a 200-mesh sieve. However, previous work has shown that equality of fineness, as measured by a given sieve, is not a proper criterion of equality of effective fineness for cements of varied composition and physical characteristics, even when the same mill and grinding media are used throughout. A better measure of effective fineness is the specific surface—that is, the total surface of all the particles in unit weight of cement. The specific surfaces of all the cements produced in this investigation were determined by means of a sedimentation device developed at this laboratory.

Preparation and Storage of Cement Pastes

Three hundred grams of cement and 120 ml. of distilled water were mixed and stirred vigorously for several minutes by a high-speed motor-driven stirrer, at the end of which time the paste was put into ten glass phials. The phials

TABLE I.—RESULTS OF EXPERIMENTS.

Cement.	Clinker Temp. during Burn.	Clinker Analysis.					Clinker Compounds Calcd.				Gypsum added.	Cement Sp. Surface.	Initial Heat of Soln.	Heat of Hardening Neat Cement with 40% Water.†				
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	$4CaO.Al_2O_3.Fe_2O_3$	$3CaO.Al_2O_3$	$2CaO.SiO_2$	$3CaO.SiO_2$				3 days.	7 days.	28 days.	90 days.	180 days.
	°C.*	%	%	%	%	%	%	%	%	%	%	sq.cm./g.	cal./g.			Calories per gram.		
2122	1,400	27.7	3.8	2.0	2.5	65.0	6	7	60	26	3.2	1390	588.7	51.2	53.1	72.5	81.2	78.5
2123	1,400	26.0	3.5	5.1	2.3	63.1	15	1	52	29	3.2	1450	575.7	40.6	45.7	61.0	71.9	74.3
2092	1,440	21.9	5.7	2.8	5.0	65.0	8	11	20	56	3.2	1470	623.6	74.8	84.7	92.2	100.6	104.8
2088	1,400	24.6	5.8	2.8	2.4	64.2	8	11	47	31	3.2	1480	595.5	53.2	63.1	73.7	77.7	87.6
2096	1,450	25.0	3.9	2.1	2.4	66.6	6	7	33	52	3.2	1500	604.5	71.9	78.8	88.8	92.6	95.9
2085	1,400	22.3	6.2	2.8	2.4	66.5	9	11	22	55	3.2	1530	618.8	77.5‡	90.3	101.0	103.7	109.2
2086	1,400	22.3	6.2	2.8	2.4	66.5	9	11	22	55	4.3	—	611.6	73.3	91.5	97.7	103.3	108.0
2087	1,400	22.3	6.2	2.8	2.4	66.5	9	11	22	55	3.2§	—	623.0	79.1	91.5	96.3	104.1	110.2
2094	1,500	20.9	4.6	5.7	2.1	66.3	17	3	6	71	3.2	1560	610.0	77.3	87.5	92.4	100.5	102.7
2124	1,400	23.5	4.8	7.2	2.2	62.0	22	1	44	31	3.2	1570	573.0	42.1	46.8	61.5	70.0	72.5
2089	1,400	22.0	4.6	6.1	2.3	64.1	18	2	22	54	3.2	1580	599.0	64.7	77.9	85.8	90.1	93.1
2090	1,400	21.4	8.8	1.2	2.5	66.6	4	21	26	47	3.2	1540	633.4	89.5	96.6	108.8	114.1	115.9
2093	1,400	21.4	8.8	1.2	2.5	66.6	4	21	26	47	6.5	1600	611.1	90.6	95.2	106.4	108.7	114.0
2125	1,400	22.5	5.0	7.5	2.2	62.7	23	1	34	40	3.2	1620	585.9	58.8	62.8	74.2	78.1	83.8
2095	1,400	21.3	6.1	2.9	2.6	67.0	9	11	12	66	3.2	1630	625.6	84.8	94.5	103.7	107.5	113.3
2091	1,500	21.9	5.6	2.7	2.4	67.7	8	10	12	68	3.2	1670	624.0	84.0	91.3	99.9	106.2	109.4
2170	1,400	25.7	4.1	6.1	2.1	61.0	18	1	61	17	3.2	1530	564.7	28.3	36.3	49.8	—	—

* ± 15° C.
† At 35° C. (95° F.).
‡ Average value, two tests.
§ Added as gypsum and converted to plaster of Paris by heating at maximum temperature of 150° C. after milling (determined by loss of weight).

were immediately stoppered with corks and sealed with paraffin wax. All ten phials were then placed in a constant-temperature cabinet maintained at 95 deg. F. where they remained until required for heat of solution determination. The storage temperature of 95 deg. F. approximates to the average mean temperature of mass concrete during the early part of its existence.

Determination of Heat of Solution

At the end of the required curing period, one of the phials was removed from the constant-temperature cabinet, the glass was broken off the hardened cement, and the latter broken up and ground as rapidly as possible in a mortar to a fineness such that all the material would pass a 100-mesh sieve. The sample was thoroughly rolled, and a portion of it placed in a weighing bottle. The bottle and contents were weighed, and two samples removed successively therefrom. One sample weighing approximately 7 grams was placed in a second weighing bottle, to be dissolved in the calorimeter; a second sample (about 3 grams) was placed in a weighed platinum crucible for determination of loss on ignition. Since these ground materials tend to lose weight rapidly, the weight of the original weighing bottle and contents was determined after removal of each of the two samples.

The smaller sample was kept at about 900 deg. C. in an electric muffle overnight, and was cooled and weighed the following day. This long ignition period was found necessary. The larger sample was dissolved in the calorimeter, and its heat of solution calculated from the observed temperature rise, corrected for all significant heat transfers during the experiment. The heats of solution of the dry cements were determined in an analogous manner.

Experimental Data Obtained

The essential data are given in Table I. Each raw mixture had been proportioned to produce a clinker of definite composition, but, inasmuch as there were small differences between the estimated analyses and those found experimentally, it is the latter which were made the basis of further study and which are given in the Table.

The clinker compounds were calculated in accordance with the findings of Bogue and his staff. The amount of free lime left in the clinkers after firing was zero in all cases except one. In this case (cement No. 2095) the amount was 0.03 per cent., a negligible quantity. A study of the figures in Table I shows the following wide ranges in calculated compound composition:

	%
Tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$) ..	3.6–22.7
Tricalcium aluminate ($3CaO.Al_2O_3$)	0.6–21.3
β-Dicalcium silicate ($2CaO.SiO_2$)	6.2–61.1
Tricalcium silicate ($3CaO.SiO_2$)	16.7–71.3

All the compositions, except that of cement No. 2092, were designed to have 2.5 per cent. magnesia. Their variations, with this exception, are only such as were occasioned by the experimental and analytical errors. The value

was doubled in the case of cement No. 2092 in order to obtain an independent indication of the effect of this oxide by comparison with cement No. 2085 which was designed to be of the same proportional composition in everything else. According to Bogue, the magnesia remains essentially uncombined. Heat data are reported for ages up to six months. It is proposed to continue the study and obtain data at one and two years as the specimens attain these ages.

All cements were prepared by grinding with the same amount of gypsum, with the exception of samples Nos. 2086, 2087, and 2093. The former two were prepared from the same clinker as was cement No. 2085 and show, respectively, by comparison with it the effect of a larger amount of ground-in gypsum and of alteration of gypsum to plaster of Paris, a change which must occur to some extent in much commercial practice because of the temperatures which the mills often reach. Cement No. 2093 is a part of cement No. 2090 to which further gypsum was added in an attempt to improve its setting properties. The mixing was effected by additional milling, using solid rubber balls which have negligible grinding action. In spite of the increase in retarder the cement remained very quick-setting, and partially set during the preparation of the paste, as had sample No. 2090.

Because of the laboratory method of preparation, all of these cements gave less residue on the 200-mesh screen than is generally the case with commercial cements of the same specific surfaces. This residue was in all cases less than 1 per cent. The surface values correspond to good commercial practice. A moderate range resulted from the milling schedule which was employed. The surface analysis is considered to be reproducible to about ± 1.5 per cent.; larger divergences were probably caused for the most part by the lack of a sensitive control over the operation of the preliminary pulveriser. Also, the differences in chemical composition probably had some effect upon the facility of grinding.

The initial heats of solution are those which were obtained with the unreacted cement. The heats of solution obtained with the reacted cement at the various ages were, thus, these values minus the quantities which are reported as heat of hardening and which were obtained by the reverse calculation.

Method of Mathematical Analysis

Fourteen clinkers are represented by the cements of Table I. Omitting cements Nos. 2086, 2087, and 2093, which were prepared from the same clinkers as others of the series but with variations in the amount or nature of the retarder, there remain fourteen cements, one for each clinker. Of these, sample No. 2170 was prepared so late that the 90-day data are still lacking. Consequently, it is desirable to disregard it for the time being, leaving thirteen cements, corresponding to thirteen widely different clinkers, for which the heats of hardening for 3, 7, 28, 90, and 180 days have been determined.

These thirteen cements and the heats of hardening which were found for them have been subjected to mathematical analysis by the method of least squares to obtain the contribution made by each per cent. of each compound

to the total heat of hardening, on the assumption that the heat of hardening for each cement at each age can be represented by the linear relationship

$$k_1\ (\%\ 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3) + k_2\ (\%\ 3CaO{\cdot}Al_2O_3) + k_3\ (\%\ 2CaO{\cdot}SiO_2) + k_4\ (\%\ 3CaO{\cdot}SiO_2) = \text{heat evolved per gram cement}$$

in which the percentages are those in cement and the k's are constant for any given age and method of making and curing the specimens, and for any Portland cement composition, irrespective of the relative proportions of its compounds.

In other words, after carrying through an analysis on the thirteen cements at a given age, there are obtained on this basis four constants which represent, respectively, the heat evolved by 0.01 gram of each of the four compounds. Or they may be expressed as the contribution of each per cent. (on weight of cement) of each of the four compounds to the heat evolved during the hardening of one gram of cement. The stated assumption neglects to take into account the effect of the gypsum and of the magnesia. Variation in the amount of the former had been indicated by the tests already discussed to be without effect. Although it may still have an effect, but one which is relatively insensitive to change, there is no way of evaluating it from the data at hand, since the gypsum is present in all of the cements and is in constant amount in those chosen for this analysis. Moreover, since in commercial practice it is added to nearly every cement in about this amount, the result of allowing its effect to be absorbed into those reported for the other compounds would scarcely interfere with the practical utility of the values obtained.

As regards magnesia, in a preliminary analysis a constant for this oxide was carried as an unknown to be determined the same as for the other compounds; but, owing to the fact that the magnesia had been intentionally varied in amount in only one cement, and the actual variations (indicated by chemical analysis) in the other cements were slight, the values obtained for the various ages were no greater than their probable errors. Thus, for the group of thirteen the values were:

Days.	Calories.	Days.	Calories.
3	-0.4 ± 1.1	28	-0.5 ± 1.1
7	0.0 ± 1.0	90	$+0.9 \pm 1.0$

There is no obvious trend with age, and the average value is zero, which makes it appear that in the mathematical analysis the magnesia merely acted as a means to reduce the effect of chance discrepancies. Since in this capacity it would tend to alter slightly the best values of the other compounds for general use, it was eliminated from the mathematical analysis. The comparison already reported between cements Nos. 2085 and 2092 indicated a negative value for the effect of magnesia, but the data are too meagre to warrant assigning a numerical value to it on that basis. Whatever its real amount, the effect of its omission is minimised by its being present in only small percentages in these cements, as it also is in commercial cements.

The assumption of linearity of function is in accord with the generally accepted conception of the reaction of cement with water as proceeding without interaction between the compounds (other than the action of gypsum with the aluminates). It is obvious, however, that the distribution of the water to each per cent. of each compound could be highly dependent upon the relative proportions of those compounds in a given cement, with consequent lack of linear relationships. Perhaps it is best to recognise this assumption as a hypothesis and let it be justified by the results of the analysis.

One other matter must be given some attention here—the range in specific surface exhibited by these cements. Independent data were obtained on one normal cement composition ground to several different finenesses, and it was found that the percentage increase in heat evolution was only about half of the percentage increase in fineness even at three days. These data were obtained as a part of another investigation and will not be reported in detail here; but, if it may be assumed that the findings are roughly characteristic of the other compositions as well, the effect of the range in surface exhibited by the cements of the present series is much less than might have been suspected. Furthermore, no correlation between the specific surfaces and the amounts of the compounds is evident; to the extent that the differences in specific surface are random ones, it is to be expected that their effect would show in the magnitude of the probable errors rather than in the actual values found.

The manner of calculation consisted in employing the mathematical method of least squares. By this method the observation equations of the form presented previously were reduced to only four weighted equations. These derived equations, being equal to the number of unknowns to be determined, were then solvable by successive elimination of unknowns. The probable errors of the values thus obtained were calculated by use of the weights which analysis of the derived equations showed them to possess. The probable error as here used is defined as an error of such a magnitude that the probability of making an error greater than it in any given observation is equal to the probability of making one less than it. The method conformed throughout to standard practice in the adjustment of unconditioned indirect observations of equal weight. (The heat evolutions determined for each cement were considered to be of equal weight.)

Since cement compositions are generally reported only in terms of the oxide composition, the necessity of calculating the compounds renders desirable the interpretation of the heat data in terms of oxide composition. Such an alternate treatment is also desirable from certain viewpoints simply because it avoids the theory of the mineralogical constitution of clinker. Since the percentage of each compound is a linear function of the percentages of the oxides the desired transformation may readily be made. The results are shown in Table II. In applying these data to cements, the percentage of lime must be corrected for lime present in the retarder as calcium sulphate.

TABLE II.

HEAT OF HARDENING IN TERMS OF OXIDE COMPOSITIONS.

Contribution of Each % in Cement to Heat Evolution of 1 Gram of Cement.

Oxide.	3 days. Cal.	7 days. Cal.	28 days. Cal.	90 days. Cal.	180 days. Cal.
CaO	+3.40	+3.92	+3.31	+3.28	+3.29
SiO_2	−5.79	−6.80	−4.93	−4.55	−4.65
Fe_2O_3	−3.2	−3.2	−3.1	−2.9	−2.6
Al_2O_3	−1.1	−1.5	−0.1	−0.4	+0.4

The amount to be subtracted is 0.7 times the amount of SO_3 which is reported in the analysis. Any uncombined or free lime should also be subtracted if it can be determined. The effect of free lime on the heat evolution has not been determined experimentally, but, to the extent to which it has hydrated or carbonated prior to the use of the cement, it probably has no very direct effect. Its presence, however, indicates that there is more dicalcium silicate and less tricalcium silicate than would otherwise be the case, and this situation is taken care of by subtracting the free lime from the total lime. The values in Table II are not offered as applicable when, owing to wider variation in the relative amounts of oxides, compounds are formed other than those actually present in the compositions here studied.

These results are not offered as a means for the accurate prediction of the heat evolution of a commercial cement of indefinite history, used under any given conditions. But for the conditions under which they were determined they show the heat effects of the major clinker compounds which are believed to be formed; to the extent to which it may be assumed that the same order will be maintained under altered conditions, they show in general the relative effects of these compounds. Although other factors enter to modify the heat evolution of an actual commercial concrete, it is the chemical compounds which are responsible for that evolution; a knowledge of their relative contributions under definite conditions is the first essential in the design of more suitable cement compositions for use where this property is important.

The following conclusions, applicable to the conditions maintained in the experiments, are drawn from this study:

(1) Portland cements continue to evolve heat during hardening for a period of six months (and probably longer).

(2) A considerable portion of the heat has been evolved at the end of three days, and the order of sequence for different cements which obtains at that time is in general maintained throughout the six-month period.

(3) Pronounced changes in the proportions of the cement raw mixture, and hence in the compounds present in the clinker, produce marked differences in heat of hardening. (Of those cements in this series for which complete six-month data are available, the range at three days is from 41 to 91 calories per gram, and at six months from 73 to 116 calories per gram.)

(4) The compounds, ranked in descending order on the basis of the heat evolution during the first three days, are first, tricalcium aluminate, then tricalcium silicate considerably lower in heat evolution, and finally tetracalcium aluminoferrite and β-dicalcium silicate with relatively small values quite close together. Considering the latter two as occupying practically the same position, this order is maintained at the later ages.

(5) The predominant values for the tricalcium compounds and the close agreement between those for the other two compounds permit the heat evolution of fresh cements, similarly prepared, to be estimated on the basis of the former compounds alone. Thus, for the experimental cements the function (percentage $3CaO{\cdot}SiO_2$) + 2.1 (percentage $3CaO{\cdot}Al_2O_3$) exhibits good correlation with the heat evolution.

The heat evolution may be estimated with equal accuracy either from the calculated percentages of the various compounds or directly from the analysis of the cement expressed in terms of the oxides, and the constants have been given for both methods.

"Reinforced Concrete Reservoirs and Tanks"

By W. S. GRAY, B.A,, M.A.I., A.M.Inst.C.E.I.

200 Pages, 119 Illustrations.

CONTENTS

Chapter
- I—Circular Tanks.
- II—Gasholder and Tar Tanks.
- III—Shallow Circular Tanks of Large Diameter.
- IV—Open Reservoirs.
- V—Reservoirs with Counterforted Walls.
- VI—Open Rectangular Tanks Below Ground.
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- IX—Swimming Baths and Tanks with Sloping Floors.
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- XI—Covered Tanks.
- XII—Large Roofed Tanks in Water-logged Ground.
- XIII—Examples of Completed Reservoirs.
- XIV—Notes on Design and Construction Methods.
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For the first time in any book, valuable information is included on the design and construction of tanks in ground subjected to subsidence by mining, and on the stability of tanks in water-logged ground.

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The Hardening and Corrosion of Cement.—V.

By Dr. KARL E. DORSCH

(OF THE TECHNICAL HIGH SCHOOL, KARLSRUHE, BADEN).

The Setting Temperature of Different Cements.

VISCOMETRIC and electrical conductivity investigations on setting cement have shown that an extremely vigorous reaction begins immediately cement is mixed with water, and that this proceeds irregularly and attains approximate constancy after twelve to fifteen hours. It now appeared desirable to amplify the preceding work by a thermal investigation of the setting of cement. Thermal research on the setting of Portland cement was first briefly carried out by Nacken,[17] who measured the amount of combined water and the temperature of the setting cement and found a remarkable agreement between the two. Since Nacken did not publish the composition of the cement used in his experiments it is not possible to compare his temperature curves with the present author's viscosity

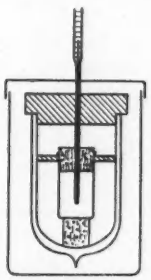

Fig. 41.—Apparatus for measuring temperatures during setting.

and electrical conductivity curves, and thermal measurements have therefore been made on the cements used in obtaining these curves. This work, like that already described, has included various kinds of cement, viz., high strength and ordinary Portland, iron-Portland, blast-furnace, and aluminous.

The apparatus is shown in Fig. 41. It consists essentially of a wide Dewar vacuum flask with double cork insulation. Inside is a cork-insulated beaker containing the cement paste under investigation. A thermometer graduated in twentieths of a Centigrade degree is inserted in the cement. The external temperature was maintained constant at 18 deg. C.

The results are given in Fig. 42; the curves are not corrected for radiation from the vacuum flask, but as this is small and constant the course of the curves is not appreciably affected. It will be seen that the temperature of all the cements rises about 5 deg. C. shortly after mixing with water. The temperature then remains constant for a period which depends on the nature of the cement—1½

[17] Nacken, *Zement*, No. 47, 1929.

hours for aluminous, 2 hours for high-strength Portland, 3 hours for ordinary Portland, 3½ hours for iron-Portland, and 4 hours for blast-furnace cement. At the end of this period the temperature rises rapidly in every case, the time of commencement of this rise coinciding with initial set as measured by the Vicat needle. Aluminous cement reaches a maximum temperature 116 deg. C. (curve I) in 5½ hours, high-strength Portland 68 deg. (curve II) in 9½ hours, ordinary Portland 56 deg. (curve III) in 12 hours, iron-Portland 42 deg. (curve IV) in 12½ hours, and blast-furnace cement 33 deg. (curve V) in 15 hours. The thermal curve for gypsum (curve VI) affords an interesting contrast. Gypsum sets a few minutes after mixing with water, with considerable rise in temperature. Before the maximum is attained a well-defined halt and inflexion in the curve can be distinguished, although this is not evident in Fig. 42. The maximum temperature in all cases approximately coincides with the final set of the cement.

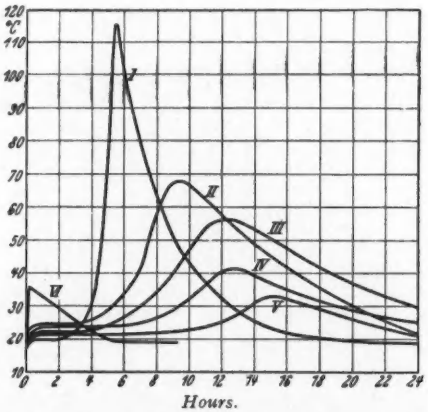

Fig. 42.—Temperature-time curves of various Cements: I.—Aluminous. II.—High-strength Portland. III.—Ordinary Portland. IV.—Iron Portland. V.—Blast-furnace Cement. VI.—Gypsum.

The high and rapidly attained maximum setting temperature of aluminous cement is to be attributed to the rapid hydration of the calcium aluminates, which proceeds with the greatest vigour: this has already been clearly shown by the electrical conductivity measurements (Fig. 39). The hydration of the calcium silicates present in Portland cement is much slower and much less heat is evolved, while the reaction begins much later than with aluminous cement. The temperature difference between high-strength and ordinary Portland cements and the sideways displacement of the maximum is due to the difference in the surface available for reaction. Owing to its greater reaction surface the temperature attained by the high-strength Portland is much higher than that of ordinary Portland. The maximum temperatures of iron-Portland (70 parts Portland and 30 parts slag) and blast-furnace cement (30 Portland, 70 slag) are much lower than for the

Portland cements and are reached after longer time. This is obviously due to the feeble activity of the blast-furnace slag contained in these cements.

Combined Water in Setting Cement.

An attempt was now made to compare the temperatures attained during the setting of the various cements with the amount of combined water, as was done by Nacken[18] for Portland cement. Nacken estimated the amount of combined water by mixing small amounts of cement with 30 per cent. water, and after determined periods heating the pats for an hour in a drying oven at 110 deg. C. The water then retained was considered to be chemically combined. This method is open to criticism in that 110 deg. is not a high enough temperature to remove completely the water held by adsorption in the gel envelopes. The amount of water evaporated in Nacken's method will depend upon the weight and surface of the cement pat. A large pat would thus retain much more " combined " water than a small one, and a spherical sample would retain more than a flat pat.

To confirm these theoretical ideas an investigation of Nacken's method of determining combined water was undertaken. Various cements were mixed with 30 per cent. water. Small quantities of the pastes, as nearly as possible equal (0.4 to 0.8 g.), were transferred on a spatula to small glass dishes which were rapidly weighed on a quick-acting analytical balance. The samples were then stored in a closet containing air maintained at 100 per cent. humidity. After different intervals of time the samples were transferred to a drying oven at 110 deg. C., in which they were heated for one hour (or for two hours in the later experiments) and then reweighed. Although hundreds of these experiments were carried out the results could not be reproduced in a single instance.

The reason for the negative result of these measurements lies in the adsorption of water in the gel envelopes, this adsorbed water being only partly removed at 110 deg. The accuracy of this view was confirmed by heating cement pats repeatedly to 110 deg. C. until they attained constant weight, then grinding them very fine in a mortar and again heating to 110 deg. The result was a further loss of water, the magnitude of which increased with the size of the original pat.

Only one fact emerges with certainty from these experiments on combined water, viz., that there is considerable combination with water in the first few hours of setting. One hundred parts by weight of Portland cement combine under the conditions of experiment with two to four parts of water in the first day, while with aluminous cement the combined water is approximately three times as great. The amount of combined water varies with different cements. Whether these values correspond to chemically combined water, or whether they also include water held in the gel by adsorption, must be decided by further research. A suitable method of investigation is offered by the determination of vapour pressure isothermals on setting and hardened cements.[19]

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[18] Nacken, *Zement*, No. 44 (1927), Nos. 47, 48 (1929).
[19] St. Giertz-Hedström, *Zement*, No. 32 (1931).

The Solubility of Portland Cement in Water.

In discussing the electrical conductivity and the temperatures attained during the setting of cement reference was frequently made to the formation of $Ca(OH)_2$. It is now necessary to investigate whether $Ca(OH)_2$ is the only substance formed when cement and water are brought together, or whether other water-soluble compounds are formed on setting, and in what quantities they occur in the mixing water.

The solubility of $Ca(OH)_2$ in water at 18 deg. C. was first determined and found to be 0.156 g. $Ca(OH)_2$ in 100 c.c. water. The solubility of various Portland cements in water at 18 deg. C. was next measured. Fifty grammes of cement were shaken in a shaking machine with 1,000 c.c. water in a two-litre flask. After definite times of shaking the contents of the flask were rapidly filtered on a filter pump and 100 c.c. of the filtrate were analysed. The results

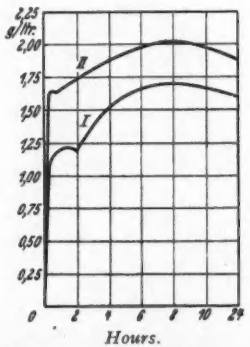

Fig. 43.—Solubility of Portland Cement in Water : I.—Ordinary Portland. II.—High-strength Portland. Ordinates represent CaO in grammes per litre.

definitely showed that the dissolved quantities of SiO_2, Al_2O_3, Fe_2O_3 and MgO were extremely small and practically independent of the time of shaking, i.e., the quantities dissolved were the same whether shaking continued for ten or a hundred minutes. This, however, is not the case for the dissolved lime. The variation in lime solubility with time for two Portland cements is shown in Fig. 43 ; the results of viscometric, electrical conductivity, and thermal measurements on these two cements are also available. Curve I was given by an ordinary Portland and curve II by a high-strength Portland cement. In addition to the difference in lime solubility, which is considerably greater for the high-strength cement, the curves show an interesting maximum in the first hour : this corresponds to the maximum value shown by the electrical conductivity measurements in the first hour. With many cements this break is not clearly defined ; instead of the maximum there may be only a point of inflexion. After this maximum is attained the lime solubility decreases somewhat and again

increases after a further half hour. In some eight to ten hours a second maximum is reached, which approximately agrees with the temperature maximum. The lime solubility then gradually falls, attaining an almost constant value after about forty-eight hours. The maxima in the lime solubility curves occur at practically the same times as those in the temperature curves, viz., in the first hour and after eight to ten hours (*cf.* Figs. 42 and 43).

It is remarkable that in the presence of cement the solubility of lime in water is considerably greater than in the absence of cement. Nacken, who also observed this phenomenon, suggested that in the presence of cement a protective colloid is formed which increases the lime solubility. The solubility again diminishes according to the degree to which this colloid is thrown down as a solid phase. Further research in colloid chemistry must show to what extent this theory may be accepted.

The Resistance of Cement to the Attack of Aggressive Solutions.

Now that the constitution and reaction of formation of cement are to a considerable extent understood, the most important problem in the chemistry of cement relates to its behaviour under chemical attack. All constructional materials are subject to slow deterioration, in which water is by far the most important factor. A cement must, for example, offer adequate resistance to the action of rain or surface water, which wash out its lime, and to the salts—chiefly sulphates—which occur in all natural waters and react with the lime and alumina. Since the work of Le Chatelier[20] and Michaelis,[21] who first realised the low resistance of cements to acids and salts, an immense volume of work in this field has been published. For the most part these publications record instances of attack on various structures, and only a few are records of systematic scientific research. Further, the results of this work are to a great degree contradictory, owing to inadequate recording of the conditions. The precise definition of the conditions of investigation is of the utmost importance in work of this nature, but the number of researches which fulfil this requirement is extremely small.

It was first necessary, therefore, to establish experimentally the conditions necessary for determining the resistance of cements to attacking solutions and to work out an unobjectionable method of experiment. As a result of this work it was found that[22] the following experimental conditions must receive strict attention.

(1) **Chemical Nature of the Cement.**—Different cements differ in their behaviour under the action of attacking solutions. Thus the lime and alumina content of the cement is of importance, and even small variations (e.g., between 63 and 65 per cent. CaO) have their effect. This is especially the case with cements of different types, such as Portland, blast-furnace, and aluminous cements. In addition to chemical composition the deterioration of a cement is considerably

[20] Le Chatelier, Congress on Research on Building Materials, Paris, 1900.
[21] Michaelis, *Tonind Zeit.*, No. 6, 1892.
[22] Probst and Dorsch, *Zement*, Nos. 10, 11 and 36, 1929; Research Bulletin of the Tech. High School, Karlsruhe, 1931.

affected by the nature of the raw materials from which it is made, by the extent to which the calcium and aluminium silicates of the raw materials are opened up by the burning process, and by the intensity of burning. An overburnt cement will be affected by salt solutions entirely differently from an underburnt cement of the same chemical analysis, and freshly burnt cement differently from the same cement after storage. These factors must all receive consideration in investigating the deterioration of cement. Chemical analysis alone obviously gives only an incomplete picture of the behaviour of cement in salt solutions.

(2) **Fineness.**—With increased fineness the surface of a cement and its reactivity increase. Cement passing the 180-mesh per inch sieve has about 2.3 times the reactive surface of a cement passing the 76-mesh sieve. Assuming that reactive surface and susceptibility to chemical attack are proportional to each other, it follows that cement passing the 180-mesh sieve is 2.3 times less resistant than the same cement which just passes the 76-mesh sieve. This extreme example shows the importance of an accurate knowledge of fineness in studying the deterioration of cement. Very finely-ground " high strength " cements which depend for their value on high initial strength are inferior from the point of view of resistance to the attack of salt solutions and would be better termed " early high strength " cements.

(3) **Added Materials.**—The nature of any material added to a cement is of importance owing to its effect on weathering and on the density of the concrete.

(4) **Density and Porosity.**—The rapidity of penetration of attacking liquids depends on the density and porosity of concrete. The greater the density the less the danger of the penetration of deleterious liquids. The density or porosity has a definite relation to the water-cement factor.

(5) **Water-Cement Factor.**—This is the percentage of water contained in the cement plus added material. If cement mortar is mixed with more water than is necessary for setting and hardening the excess water evaporates through extremely fine micropores. Attacking liquids later penetrate the material through these micropores and are thus able to set up deterioration right in the interior of the concrete. It is obvious that in comparative scientific research the nature of the mixing water must be taken into account. Tap-water is generally used. Probst and Dorsch[23] have recently shown that the mixing water has a considerable influence on strength, and their experiments prove that the use of a standard mixing water is necessary. Distilled water is recommended as the standard and the whole of the experiments described in the present work have been carried out with distilled water.

(6) **Treatment of Cement.**—The treatment of a cement immediately after mixing has a great effect upon the entire setting and hardening process. The hydration of the cement varies with the temperature of the mixing water and storage chamber and with the humidity of the latter. With high temperature of mixing water and storage chamber and low humidity, setting and hardening

[23] Probst and Dorsch, *Zement*, No. 43, 1930.

are accelerated and initial strength is increased, although the later strength is lowered. With lower temperature and higher humidity the reactions proceed more slowly, although the water penetrates more deeply into the clinker particles. The initial strength is not so high under these conditions, but the later strength is considerably increased. It is obvious that these factors will have a great influence on the behaviour of cement in contact with salt solutions. The effect of the initial conditions on the resistance of cement to chemical attack is shown by a comparison of the results of storage in moist air as against simple water or combined storage. It has been found[24]—and the author's experiments confirm this—that storage in moist air considerably increases the resistance of concrete to attacking solutions.

(7) **Length of Storage before Immersion in Attacking Solutions.**—Not only the nature of treatment after mixing, but also the time which elapses before the mortar or concrete is exposed to salt solutions is important. The attack of the solutions will be reduced as the strength attained by the concrete before immersion is increased. It is thus of the greatest importance in relation to the deterioration of concrete whether the concrete is immersed in the attacking solutions two to three days or 28 days after mixing, and whether it has been subjected to water, air or combined storage.

(8) **The Nature of the Attacking Solutions.**—It is obvious that a solution containing free acid will set up immediate decomposition of a cement. The velocity of reaction depends on the degree of dissociation of the acid. In salt solutions the acidic ions react more or less rapidly with the lime and alumina of cement, forming calcium salts, etc. The degree of decomposition of cement mortar frequently depends on the solubility of these calcium salts; the greater the solubility the greater the decomposition.

(9) **Concentration and Amount of Aggressive Solutions.**—The amount of decomposition of cement will increase with the concentration of the attacking solution, and will further depend upon the quantity of solution available. This can be demonstrated by an example. If ten test-pieces are immersed in a vessel containing 2,000 c.c. of an aggressive solution, and a further ten test-pieces in another vessel containing 4,000 c.c. of the same solution, the deterioration of the cement will be greater in the second than in the first case since there is double the quantity of salt solution available.

(10) **Surface and Size of Test-pieces.**—The total surface exposed to the attacking solution and the size of the test-pieces must be taken into consideration in determining the resistance of a cement to attack.

(11) **The Temperature of the Attacking Solution** has a great effect upon the entire progress of reaction. The velocity of reaction, and with it the rapidity with which the cement is decomposed, rise and fall in proportion with the temperature.

(12) **Storage of Test-pieces in the Attacking Solution.**—Different experimental results will be obtained according to whether the solution above the test-pieces

[24] Miller and Manson, *Public Roads*, No. 12, 1931.

is not renewed or is changed daily or monthly, whether the test-pieces are stored free from vibration and the solution is not disturbed or whether they are shaken and the solution is allowed to stream over them. In the last case the velocity of reaction is increased by the continuous supply of unused solution and the removal of the dissolved calcium salts.

The contradictory experimental results found throughout the literature of the subject are readily explained by the neglect of these simple physico-chemical factors. In the experimental work to be described in the succeeding articles these points have all received careful attention, and the results prove that it is only by taking these factors into account that scientifically comparable data can be obtained.

Book Review.

Hydrated Calcium Aluminates and their Double Salts. By C. R. Wilhelm Mylius. Mathematica et Physica VII, 3. Issued by Åbo Academy, Finland.

The publication of this work on the hydrated calcium aluminates shows that research on the hydration of Portland cement is making good progress. Some of the formulæ put forward should be accepted with reservations, particularly with respect to the number of molecules present. The work on the double salts should throw light on the action of such compounds as calcium chloride, calcium nitrate, etc., on the setting time of cement. The whole field of hydrated calcium aluminates has been explored and the results of former workers confirmed or, in some cases, corrected.

The aluminates described are:

$2CaO.Al_2O_3.7H_2O$
$3CaO.Al_2O_3.6H_2O$—$12H_2O$ – $18H_2O$
$4CaO.Al_2O_3.13H_2O$.

The double salts are:

$3CaO.Al_2O_3.3CaSO_4.31.5H_2O$
$3CaO.Al_2O_3.CaSO_4.12H_2O$
$3CaO.Al_2O_3.CaCl_2.10H_2O$
$3CaO.Al_2O_3.Ca(NO_3)_2.10H_2O$
$3CaO.Al_2O_3.CaBr_2.10H_2O$
$3CaO.Al_2O_3.CaI_2.10H_2O$
$3CaO.Al_2O_3.Ca(ClO_4)_2.10H_2O$
$4CaO.Al_2O_3.Ca(IO_3)_2.22H_2O$
$5CaO.Al_2O_3.Ca(IO_3)_2.33H_2O$
$3CaO.Al_2O_3.Ca(CH_3.CO_2)_2.8H_2O$.

A detailed description of the preparation of each compound is given which will enable other workers to obtain identical compounds when repeating the experiments.

In the chapter on constitution the author commences with the formula for aluminium hydroxide, and from this builds up the various compounds after introducing the monovalent anion $Al(OH)_4$ and the trivalent anion $Al(OH)_6$.

A good feature of the work is the inclusion of the optical properties of all the compounds. In work of this type much dependence has to be placed on the petrographic microscope, and often the optical properties are the only means of avoiding serious errors.

An excellent summary in tabular form is given, and a few notes on electrolysis of aluminate solutions are to be found at the end of the book.

A curious point to be noted is that nearly all the compounds lose water progressively on drying in a vacuum over phosphorous pentoxide ($3CaO.Al_2O_3.6H_2O$ is the exception), and in the case of $3CaO.Al_2O_3.3CaSO_4.31H_2O$ when water vapour is admitted it is reabsorbed. The process strongly resembles the action of zeolites, and it would be useful to know if there are any volume changes with the varying water content, since if there are we should have the interesting case of a crystalline substance behaving remarkably like a colloid. This may again throw light on the so-called "colloidal" character of hardened cement.

The results do not seem to have been applied to set cement as yet and we are not told whether any of these compounds have been discovered in a set and hardened specimen. The new double salts are of considerable interest, and work in this direction may shortly clear up the obscure action of certain compounds on the setting time of Portland cement.

The author is to be congratulated on having produced a very useful work which should form the starting point of a strong attack on the setting process of cement. A similar work on the silicates seems certainly to be indicated.

"False" Set of Cement.

By F. WHITWORTH (BRUSSELS).

THE extracts from an article by P. Schachtscabel in your February issue are interesting, but I must record my complete disagreement with the findings of this author. Quoting from your extract, "That this 'false' set is due to a mechanical removal of water is shown by mixing the clinker plus 4 per cent. hemihydrate with increasing quantities of water. The results with 24 per cent. water were, initial 25 minutes, final 5 hours 25 minutes; with 30 per cent. water, initial 3 hours 10 minutes, final 7 hours 25 minutes." It is my personal experience, and I believe generally accepted, that an initial set of 25 minutes is a medium fast set and has no relation to "false" set; the latter almost invariably takes place within ten minutes of gauging.

I give below the results of tests made on a sample of cement containing 2.5 per cent. SO_3. The gypsum was converted to hemihydrate by heating the cement to approximately 115 deg. C.

PER CENT. WATER.	INITIAL SET.	APPARATUS.
25	5 minutes	Vicat.
30	5 ,,	,,
35	6 ,,	,,
40	8 ,,	Pressure.

In making these tests it should be noted that with 40 per cent. water the result is a fairly thin paste, and to detect the point at which this paste loses its plasticity the usual needle tests are not sufficiently delicate (it will be of great interest, therefore, to hear more of the work being carried out by Dr. Karl E. Dorsch on the viscosity of cement during setting). The method I adopt is to make a small pat about 2 in. diameter and ½ in. deep. By lightly pressing against one side of this pat it can be clearly seen when false set has occurred. When no set has developed the pat will be seen to move not only where the pressure is applied but throughout its entire mass. When false set (or gypsum set) has developed the pat remains rigid except immediately under the finger, and when the finger is removed water will be seen to come to the surface at this point. It will be seen from these results that, contrary to what is stated by Schachtscabel, the percentage of water has practically no influence on the false set.

With reference to supersaturation of the hemihydrate and resulting retardation of the recrystallisation into gypsum, this, I believe, occurs when calcium sulphate is calcined at high temperatures of 500 deg. C. and above, and not at the temperature mentioned in these tests.

I have heated cement containing gypsum equal to 2 per cent. SO_3 content to 550 deg. C. and found the result to be a normal slow set, although the same cement gave a complete rapid set when heated to between 200 and 450 deg. C. In the first case the anhydrite had been converted into a second soluble form, a product known as " estrich gyps " ; in the second case the anhydrite had been converted into the β form and was only very slowly soluble.

From my experience " estrich gyps " is capable of retarding the setting time of cement without showing false set, although we have here supersaturation of the hemihydrate and retarded recrystallisation. It is also inconceivable that supersaturation should occur with 4 per cent. of hemihydrate present but not with smaller percentages, as reported by Schachtscabel. The results given also show a general agreement between what is called soluble anhydrite and hemihydrate, but it is not the product obtained by heating gypsum to 105 deg. C. hemihydrate and not a soluble anhydrite as claimed by Schachtscabel. According to literature on this subject the transformation temperature from gypsum to hemihydrate is 107 deg. C.

$$2CaSO_4 2H_2O \xrightarrow{107^\circ} (CaSO_4)_2 H_2O + 3H_2O$$

In view of these results I see no reason to modify the explanation for false set which has previously been published in CEMENT AND CEMENT MANUFACTURE under my name. My theory is that false set is not a setting of the cement proper, but is due to recrystallisation of the hemihydrate into gypsum, the crystals interlocking with sufficient bond to register an initial set by the needle tests unless the quantity of water added is extremely high, the cement proper meantime continuing a normal set.

Schachtscabel also remarks that rapid setting is not due to temperature rise. This is generally admitted, but on the other hand, when rapid setting occurs it is always accompanied by a sensible rise in temperature, the heat generated being an effect and not a cause of the rapid set ; false set rarely shows any appreciable increase in temperature.

From a general study of the results given by Schachtscabel I would also suggest that, where false set existed in the samples tested by him with sufficient cohesion to be recorded by the needle tests, this was probably partially or completely worked through during the gauging. Pats for testing for false set should be gauged with all possible speed, because if the hemihydrate is very finely ground the conversion to gypsum may take place very rapidly. The hemihydrate content must exceed at least 1 per cent. SO_3 equivalent, otherwise the false set is not sufficiently pronounced to be recorded by the needle tests.

The effect of alkali carbonates on the setting time is interesting, and partially bears out the explanation given by M. Candlot for certain cements becoming rapid setting on aeration ; this was commented upon in my previous contributions on this subject.

INTERNATIONAL DICTIONARY OF CEMENT.

ARRANGED BY DR. C. R. PLATZMANN, WITH COLLABORATORS IN ENGLAND, FRANCE, AND SPAIN.

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
	Q		
quality	qualité	Güte	calidad
quarry	carrière	Steinbruch	cantera
	R		
radiation	rayonnement	Strahlung	radiación
rail	rail	Schiene	carril
ram	dame, sonnette	Fallramme	mazo pisón
rapid hardening cement	ciment à durcissement rapide ; ciment special	hochwertiger Zement	cemento de endurecimiento rápido
rapid setting	prise rapide	Schnellbinden, das	fraguado rápido
raw material	matière première ;	Rohmaterial	materia primera
raw meal	poudre crue	Rohmehl	crudo
raw mill	broyeur pour matières crues	Rohmühle	molino de crudo
ray	rayon	Strahl	rayo
reduction gear	engrenage réducteur	Reduziergetriebe	reductor de engranaje
refractory	produit réfractaire	feuerfestes Material	refractario
reinforced concrete	béton armé	Eisenbeton	hormigón armado
repair	réparation	Reparatur	reparación
repair shop	atelier de réparation	Reparaturwerkstätte	taller de reparación
report	rapport	Bericht	informe
research	recherche	Forschung	investigación
residue	residu	Rückstand	residuo
resistance	résistance	Widerstand (elektr.)	resistencia
retarder	retardateur	Abbindeverzögerer	retardador
revolution	rotation, révolution	Umdrehung	revolución
revolving screen	tamis cylindrique	Trommelsieb	criba giratoria
riding ring	anneau de roulement	Laufring	anillo de rodadura
rivet	rivet	Niete	remache
rock drill	perforatrice	Gesteinsbohrer	perforadora o barrenadora para roca
roll crusher	broyeur à cylindres	Walzenbrecher	triturador de rodillo
roller bearing	palier à rouleaux	Walzlager, Laufringlager	soporte de rodillos
roller for kiln	galet du four	Ofenwalzlager	rodillos para los hornos
rope drive	commande par câbles	Seilantrieb	transmisión por cables
ropeway	funiculaire aérien	Seilbahn	transportador aéreo de cable
rotary drier	séchoir rotatif	Trommeltrockner	secador rotatorio
rotary grate shaft kiln	four vertical à grille tournante	Drehrostschachtofen	horno vertical de parrilla rotatoria
rotary kiln	four rotatif	Drehofen, Rotierofen	horno rotatorio
rotary kiln lining	garnissage du four rotatif	Drehofenfutter	revistimiento refractario del horno rotatorio
roughing mill	broyeur dègrossisseur	Rohmühle	molino preliminar
rubber	caoutchouc	Gummi	caucho
rupturing capacity	capacité de rupture	Schaltfähigkeit	capacidad de ruptura
	S		
sand	sable	Sand	arena
scratch	rayure	Schramme	huella de raya
screen	tamis	Sieb	tamiz
screw conveyor	vis, transporteuse	Schnecke, Sckraubentransporteur	transportador de tornillo
sea water	eau de mer	Seewasser	agua del mar
semi-steel	fer coulé	Flusstahl	semi-acero

(*Continued on page* 182.)

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
setting	prise	Abbinden, das	fraguado
setting-time	temps de prise	Abbindezeit	tiempo de fraguado
shaft kiln	four vertical	Schachtofen	horno vertical
shaker conveyor	transporteur à secousses	Schütteltransporteur	transportador de sacudidas
shaking (to compact)	tasser per secousses	einrütteln	asentar por sacudidas
shale	schiste	Schieferton	esquisto
sheet iron	tôle	Eisenblech	plancha de hierro
shell	tambour	Mantel (Ofen)	cubierta o envolvente
shift	poste, travail d'une équipe	Arbeitschicht	turno
shrink, to	se contracter	schwinden	contraerse
shuttle conveyor	transporteur à va-et-vient	Schütteltransporteur	transportador de sacudidas
sieve	tamis	Sieb	tamiz
silica	silice	Kieselsäure	sílice
siliceous	siliceux	kieselsäurehaltig	silíceo
slag	laitier	Schlacke	escoria
slake, to	éteindre (lachaux)	löschen	apagar
sleeper	anneau mortier	Schwelle	durmiente o traviesa
sleeve bearing	palier lisse	Muffenlager	cojinete de manguito
slide valve	tiroir	Schiebeventil	valvula corredera
sling	élingue	Schlinge	cuerda
slip ring motor	moteur à bagues	Schleifringmotor	motor de anillos rozantes
slurry	pâte, boue	Schlamm	pasta
slurry mixer	mélangeur à boues	Schlammischer	mezclador de pasta
slurry ring	anneau de boue collé au cylindre	Schlammringansatz	anillo adherente de pasta
sodium	sodium	Natrium	sodio
solubility	solubilité	Löslichkeit	solubilidad
solution	solution, liqueur	Lösung	solución
solvent	solvant	Lösungsmittel	disolvente
soundness	invariabilité, stabilité de volume	Raumbeständigkeit	estabilidad de volumen ; constancia de volumen
soundness test	épreuve d'invariabilité de volume	Raumbeständigkeit-sprüfung	ensayo de inalterabilidad de volumen
spatula	spatule	Spatel	espátula
specimen	échantillon	Probe	probeta
specific gravity	poids spécifique	spezifisches Gewicht	peso específico
specific heat	chaleur spécifique	spezifische Wärme	calor específico
speed	vitesse	Geschwindigkeit	velocidad
speed reduction	réduction de vitesse	Geschwindigkeits-reduktion	reducción de velocidad
spillage	déchet (à l'ensachage)	Abfall	pérdida, desecho
spiral conveyor	convoyeur à vis ; vis transporteuse	Transportschnecke	transportador espiral ; transportador de tornillo
spoon-fed	cuiller d'alimentation	Löffelzufuhr	alimentador de cuchara
spray feed	enfournement par pulvérisation	Sprühaufgabe	alimentación por surtidores
spring	ressort	Feder	resorte o muelle
spur gear	roue d'engrenage ; engrenage droit	Stirnradgetriebe	engranaje recto o cilíndrico
spur rim	jante à denture droite	Zahnkranz	corona dentada
squirrel-cage motor	moteur à cage d'écureuil	Kurzschlussmotor	motor de jaula de ardilla
stainless steel	acier inoxydable	rostfreier Stahl	acero inoxidable
standard coal	charbon normal	Normalkohle	carbón tipo
standard sand	sable normal	Normalsand	arena normal
standard specifications	nomenclatures	Normen	normas
star-delta type	type étoile triangle	Sterndreieckstyp (elektr.)	tipo de estrella triángulo

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
starter	démarreur	Anlasser	arrancador
starting torque	couple de démarrage	Anlassdrehmoment	par de arranque
steam	vapeur	Dampf	vapor
steam engine	machine à vapeur	Dampfmaschine	máquina de vapor
steam navvy	excavateur à vapeur	Dampfbagger	pala mecánica
steel	acier	Stahl	acero
steel band conveyor	convoyeur à bande d'acier	Stahlbandtransporteur	transportador de cinta de acero
stirrer	agitateur	Rührwerk	agitador
stirring gear	dispositif d'agitation	Rührgetriebe	dispositivo amasador
stoppage	arrêt	Stillegung	paro
storage tank	bassin d'attente	Lagerbehälter	silo de almacenaje
store	entrepôt	Vorratslager	almacén
strength	résistance	Festigkeit	resistencia
stuffing box	presse-étoupe	Stoffbuchse	prensa estopas
suction	aspiration	Saug (zug)	aspiración
sulphur	soufre	Schwefel	azufre
sulphuric acid	acide sulfurique	Schwefelsäure	ácido sulfúrico
super-cooled	refroidi	unterkühlt	sub-enfriado
superheat, to	surchauffer	überhitzen	recalentar
superheater	surchauffeur	Ueberhitzer	recalentador
supersaturated	sursaturé	übersättigt	sobresaturado
support	support	Lager (Kugel- etc.)	apoyo
surface	surface	Oberfläche	superficie
surface tension	tension superficielle	Oberflächenspannung	tensión superficial
surplus	excès	Ueberschuss	exceso
swinging conveyor	convoyeur rotatif, basculeur	Schwingtransporten	transportador de impulsión
switch	commutateur	Schalter	interruptor
switchboard	tableau de distribution	Schalttafel	cuadro de distribución
switchgear	interrupteur	Schaltgetriebe	interruptor
		T	
table feed	plateau d'alimentation	Telleraufgabe	mesa de alimentación
tap water	eau potable	Trinkwasser	agua ordinaria
tempering	tempe	Tempern	temple
tensile strength	résistance à la traction	Zugfestigkeit	resistencia a la tracción
test, to	essayer	prüfen, untersuchen	ensayar
testing	essai	Prüfung, Versuch	ensayo
testing machine	machine à essayer	Prüfmaschine	aparato de ensayo
test sample	éprouvette	Probekörper	probeta
thermo-couple	thermo-couple	Thermoelement	termo-par
thermo-electric pyrometer	pyromètre thermo-électrique	thermoelektrisches Pyrometer	pirómetro termo-eléctríco
thick slurry process	procédé à pâte épaisse	Dickschlammverfahren	proceso de pasta espesa
thin section	section mince	Dünnschliff	sección delgada
three phase current	courant triphasé	Dreiphasenstrom	corriente trifásica
three chamber mill	moulin broyeur à trois chambres	Dreikammermühle	molino de tres cámaras
three throw pump	pompe à 3 pistons	——	bomba de tres tiempos
throttle valve	vanne papillon	Winddrosselschieber	válvula de cuello
tine	denture	Zacke, Zahn	entalladura
tippler	basculeur	Kippvorrichtung	volcádor
tippler truck	wagon à caisse basculante	Kippwagen	vagoneta volquete
titrate, to	titrer	titrieren	valorar
titration	dosage	Titration	valoración
toggle joint	biellette articulée	Gelenkverbindung	junta articulada
ton	tonne	Tonne	tonelada
tool	outil	Gerät, Werkzeug	herramienta
transition point	point de transformation	Umwandlungspunkt	punto de transición

(*Continued on page* 184.)

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
travelling crane	pont roulant	Laufkran	grúa móvil
travelling grate	grille mécanique	Wanderrost	parrilla transportadora
tray conveyor	transporteur à augets	Kastentransporteur	transportador de artesas
trip gear	limiteur de course	Ausklinkvorrichtung	mecanismo de desenclavamiento
tripod	trépied	Dreifuss	tripode
trough	auget	Rinne, Trog	artesa
troughed band conveyor	convoyeur à bande en auget	Förderrinne	transportador de canales
trowel	cuiller, truelle	Kelle	paleta, llana
trunnion	tourillon	Zapfen (Welle)	muñón
tube	tube	Rohr	tubo
tube mill	tube broyeur	Rohrmühle	refino tubular
turbine blade	ailette de turbine	Turbinenflügel	aleta de turbina
turbo-generator	turbo-alternateur	Turbogenerator	turbo generador
turntable	plaque tournante	Drehscheibe	plataforma rotatoria
twenty-eight days duration	durée de 28 jours	Zeitraum von 28 Tagen	duración de 28 dias
		U	
underburnt material	incuits	Leichtbrand	material mal cocido
uniflow steam engine	machine à equicourant	Gleichstromdampfmaschine	máquina de vapor de simple expansión
use	usage	Verbrauch	aplicación
		V	
valve	valvule, soupape	Ventil	válvula
valve bag	sac à valvule	Ventilsack	saco con válvula
vapour pressure	tension de la vapeur	Dampftension	tensión del vapor
velocity	vitesse	Geschwindigkeit	velocidad
Vicat needle	aiguille de Vicat	Vicatnadel	aguja de Vicat
void	vide	Hohlraum	hueco
volatile matter	matière volatile	flüchtige Substanz	material volatil
voltage	tension	Spannung (elektr.)	voltaje
volume change	changement de volume	Volumenänderung	cambio de volumen
volume constancy	constance de volume	Raumbeständigkeit	estabilidad de volumen
vulcanite ring	bague en ébonite, bague en caoutchouc durci	Hartgummiring	anillo ó aro de goma endurecida
		W	
warehouse	entrepot	Lagerhaus	almacén
washmill	broyeur humide	Waschmühle	molino desleidor
waste heat	chaleur perdue	Abhitze	calor perdido
waste heat boiler	chaudière à chaleurs perdues	Abhitzekessel	caldera de recuperación de calor
water	eau	Wasser	agua
water tube boiler	chaudière aquatubulaire	Wasserrohrkessel	caldera de tubos de agua
water jacketed furnace	four à water-jacket	Wassermantelofen	horno con camisa de agua
wear	usure	Abnutzung	desgaste
wear and tear	détérioration	Verschleiss	deterioro por desgaste
weighbridge	pont à bascule	Brückenwaage	báacula-puente
weigher	machine à peser ; bascule automatique	Waage	pesador, poidómetro
weight	poids	Gewicht	peso
weight per litre	poids par litre	Litergewicht	peso por litro
weld, to	suer, souder	schweissen	soldar
wet process	procédé par voie humide	Nassverfahren	proceso de vía húmeda
Wheatstone circuit	pont de Wheatstone	Wheatstonesche Brücke	puente de Wheatstone

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
wheel	roue	Rad	rueda
wide	large, largeur	breit	ancho
winch	treuil	Winde	torno, cabrestante
wire	fil	Draht	hilo, alambre
wire triangle	trépied en fer, triangle	Drahtdreieck	triángulo de alambre
withdraw from the mould, to	démouler	entformen	desmoldear
wooden keg	baril en bois	Holzfass	barril de madera
work	usine	Werk, Fabrik	fábrica
worm gear	réducteur à vis sands fin	Schneckengetriebe	engranaje de tornillo sin fin
wrought iron	fer puddlé ; fer battu	Schmiedeeisen	hierro forjado ; hierro batido
		Y	
yield point	limite d'élasticité	Elastizitätsgrenze	límite de elasticidad

[French-English-German-Spanish, German-English-French-Spanish, and Spanish-English-German-French dictionaries for the cement industry will be published in future numbers.]

British Standard Industrial Sieves and Screens.

A BRITISH Standard Specification has just been issued for square mesh woven wire and round hole perforated plate sieving materials for industrial purposes. This specification provides for the more commonly used forms of woven wire and perforated plate and has a wide industrial application. So far as woven wire is concerned it has been found necessary to include two series of woven wire which are characterised by (1) clear mesh sieves in which the size of the aperture is expressed in inches or fractions of an inch, and (2) the number of meshes per linear inch, this series containing sieves ranging from 300 meshes to the inch down to four meshes to the inch.

It has been found practicable to standardise perforated plates other than those having round holes staggered at 60 deg. Two series of perforated plates have been provided, a heavy series with holes from 3 in. to $\frac{1}{16}$ in. diameter, and a light series with holes from 1 in. to 0.029 in. diameter.

In consequence of the great variety of lengths and widths used in industry, it has not been found practicable to standardise overall dimensions of woven wire or perforated plates. Attention is drawn, however, to the fact that woven wire is generally stocked in widths of 24 and 36 in., with a selvedge on both sides, and in certain meshes in widths of 21, 22 and 40½ in. for supply to particular industries. The material used in the manufacture of woven wire depends on the purpose for which it is required. It cannot therefore be standardised, but is normally stocked by makers as follows: steel, up to 90 mesh; copper, up to 100 mesh; brass, up to 200 mesh; phosphor bronze, up to 300 mesh.

It has been found impracticable at the present stage to lay down tolerances for the standard sizes of apertures either for woven wire or perforated plate. The co-operation of manufacturers and users is invited in this matter, so that the revision of the specification in this direction may be possible after one or two years' experience has been gained.

The Committee responsible for the preparation of this specification included representatives of Government departments, the cement industry, scientific institutions, and industrial associations. Copies of the specification (B.S.S. No. 481–1933) can be obtained from the British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d. by post.

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